FLAME RETARDANTS AND THEIR APPLICATION TO TEXTILES*

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FIRE is constructively involved in some way in almost everything we do. This is truly paradoxical. We should not have the high standard of living that we now enjoy were it not for combustion. Yet fire, uncontrolled, destroys millions of dollars of property annually.[1]

There is no estimate of the extent of personal injuries and losses that are due to the ignition of textiles, but the figure is certainly very high. Fire prevention is the positive approach to reduction of these injuries and losses. A number of organizations have been active in the search for flame retardants for cellulosic fibers that would be both effective and durable for the useful life of the fabric.

Efforts to make textiles flame-resistant are not new,[2] but early research investigations were limited to the use of water-soluble compounds. For example, such substances as borax, boric acid, diammonium phosphate, and ammonium sulfamate impart resistance to flame but, because they are water soluble, the fire retardant finishes are removed by washing. Several such treatments[3] are still valuable for domestic use where nondurable flame resistance is sought for such items as curtains, draperies, potholders, and upholstery padding. For example, one effective domestic treatment uses 7 ounces of borax and 3 ounces of boric acid dissolved in 2 quarts of hot water. Cotton items are thoroughly wetted with the solution and dried by any convenient means.[3] Given this or similar treatment, cotton will be flame-resistant until wet or washed.

The most widely used flame-resistant finish for cotton in industrial

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applications is of the antimony oxide chlorinated paraffin type; vinyl chloride is sometimes added. A combination of such chemicals is applied to tents, tarpaulins, and other outdoor products, and is durable throughout the service life of these products. It is known as FWWMR (flame, water, weather, and mildew resistant) treatment. This finish adversely affects the "hand" (or feel), the drape, flexibility, and the color of the fabric, since additions up to 60 per cent are required in many cases to obtain adequate durability of the flame-resistant treatment.

The task of developing an effective durable flame-retardant finish for cotton is difficult because of the many requirements the finish must meet. To be satisfactory for most uses, a flame retardant must: 1) be easy to apply, preferably with existing finishing equipment from a water solution; 2) be effective with few additives to avoid excessive increases in weight; 3) produce a finish durable to laundering and dry cleaning; 4) leave the fabric air-permeable; 5) be physiologically inactive; 6) render the fabric resistant to afterglow; 7) not stiffen the fabric appreciably; 8) cause little or no loss in strength; and 9) be reasonable in cost.

The products and potential markets for flame-resistant fabrics are large and varied. In 1963, a total of 19 million pounds of cotton was utilized in fabric with flame-resistant finishes, both durable and non-durable. Of this, approximately one half of the finish was FWWMR. An annual potential for fire-resistant finishes on woven cotton fabrics has been estimated as equivalent to 354 million pounds. Since only 19 million pounds were actually finishes, this leaves an unfilled potential of 335 million pounds of cotton. In addition, if cotton were to capture some of the market now held by synthetics, possibly another 422-million pounds could be finished.[18]

The largest estimated potential market of 551 million pounds is for household items, such as bedding, blankets, sheets, curtains, drapes and slip covers. Industrial uses, estimated at 172 million pounds, are for such items as automobile covers, upholstery, tops, awnings, tents, mail bags, umbrellas, and other products requiring heavy textiles. The apparel market, estimated at 52 million pounds, is composed primarily of night wear, dressing gowns, work clothes and uniforms. This market potential is for the consumption of cotton in uses in apparel whose flame resistance is desirable with no increase in cost. The potential market for apparel falls off very rapidly with increasing cost; adding the flame retardants makes some of the changes in properties of fabrics unacceptable. However, the fire-resistant finishes of today are more effective, more durable, and better suited to the entire market than were the finishes of the past.[18]

The major breakthrough in the development of a satisfactory, durable, flame-retardant finish for cotton was made at the Southern Regional Research Laboratory about 1950 when tetrakis (hydroxymethyl) phosphonium chloride, known as THPC, was used. Reeves and Guthrie[4] found that THPC would react with and make aminized cotton flame retardant. Later the reaction of cotton with THPC and other substances, such as melamine urea, was studied in an effort to eliminate the aminization of the cotton. It was found that THPC reacts and polymerizes with methylolmelamine as well as with many other substances, and can form insoluble polymers inside the cotton fibers to produce good flame-resistant finishes. Simultaneously, this process involves some cross-linking of the cellulose chains in cotton.

A typical formulation that gives satisfactory results on 8-ounce fabrics contains 16.4 per cent THPC, 3.0 per cent triethanolamine, 9.4 per cent trimethylolmelamine, and 9.8 per cent urea based on the total weight of the solution. The treatment can be applied with standard chemical-finishing equipment. The solution is applied to fabric with a padder, using a tight squeeze-roll pressure. The fabric is then dried, cured at an elevated temperature, and washed by any of the usual washing procedures. A softener used to reduce stiffness and improve strength may be applied with the treating formulation or applied as a separate step in treating the fabric. This process was commercialized in 1956; several finishing mills in the United States and England are now using processes based on it for making fire-resistant cotton fabric. Much of the durable flame-resistant cotton fabric produced in the United States contains the THPC-amide finish or some modification of it. This finish is effective on most cotton fabrics of loose weave, and on heavier fabrics, that is, fabrics weighing 6 ounces or more per square yard. It is also satisfactory on some fabrics of lighter weight and of loose construction: for example 3/3 steep twill of about 4 ounces per square yard. Typical additives range from 18 per cent to 28 per cent, depending upon fabric weight, the resin system used, and the durability required. THPC resin systems are amenable to vat-dyed fabrics and may be used as the bonding agents for pigment-dyed fabrics. A textile treated with this finish withstands laundering and, in addition to being flame-resistant, is glow-resistant and imparts considerable resistance to rot and mildew. The main disadvantages of the process are cost, stiffness imparted to some fabrics, and formaldehyde odors liberated during the curing operation. Treatment of fabric with a wash-wear finish prior to treatment with this flame-retardant finish may improve the efficiency of the process and the hand of the fabric.[5]

It was determined later that the chemical fixation of a water-soluble precondensate of THPC and amides in cotton fabric with ammonia and ammonium hydroxide has certain advantages. This technique, referred to as the ammonia cure method, tends to reduce loss of the strength of a fabric associated with the heat-cure method. The improved strength imparted by this method may be due to less cross-linking of the cellulose and, to a lesser extent, to the lower temperature of resin, as compared to the heat cure method. A THPC finish using ammonia cure is in commercial production in England under the name of Proban.[6, 7] It has been reported that an improved precondensate can be obtained by incorporating diammonium sulfite monohydrate and sodium acetate in the formulation and then drying the wetted fabric and fixing the finish in ammonium hydroxide.[18]

According to the literature the disadvantages of stiffness and loss of strength in fabrics treated with the THPC formulation can be reduced by adding a methylol-substituted triazone or triazine or a cyclic ethyleneurea and also by adding a polyvinyl chloride resin with a softening point of between 170° to 200° C. A typical formulation is: 6 to 20 per cent THPC, 3 to 12 per cent of the methylol compound, 1 to 4 per cent tertiary amine, 3 to 12 per cent urea, 7 to 25 per cent PVC resin and water added depending upon the solids content desired. The solution is applied to cotton by a padding technique, and the cotton is then dried and cured for 10 seconds at 370° C. and afterwashed.[8, 9]

In October 1956, scientists of the Southern Utilization Research and Development Division announced one of the most effective and durable flame retardants: APO-THPC. APO is the abbreviation for tris (1-aziridinyl)phosphine oxide. The polymer from APO-THPC imparts a very durable flame-resistant finish with an additive relatively low in resin, and is satisfactory for use on all-cotton fabrics with the exception of tightly constructed lightweight fabrics and those weighing less than about 3 ounces per square yard. There still exists a need for an adequate flame retardant for lightweight fabrics such as sheers and nets. The APO-THPC finish is best on fabrics weighing 6 ounces per square yard and heavier. It is somewhat less than completely satisfactory on print cloth and other lightweight goods weighing less than 4 ounces per square yard. Satisfactory flame resistance can be obtained with comparatively little resin additive (8 to 12 per cent) to heavier fabrics, but more (15 to 18 per cent) is required for lighter fabrics which stiffen and weaken in the process. The finish is effective also on rayon, wool, and silk, and on blends of these fabrics, but not on cellulose acetate, nylon, or polyester fibers.[10, 11, 12, 13]

This treatment can be applied readily to cotton by use of commercial equipment. Essentially the treatment consists of padding the fabric through an aqueous solution of APO-THPC, drying at a relatively low temperature, curing it at an elevated temperature to form a highly cross-linked resin within the fibers, and then washing and drying the cotton.

APO-THPC-treated fabrics with approximately 15 per cent additive withstand repeated laundering and dry cleaning. Char length in the standard vertical flame test is about 3 inches for most fabrics.[16] Treated fabrics pass the 180° strip angle flame test[14] before and after washing. After softening, the fabric retains about 90 per cent of its breaking strength and a high percentage of its tearing strength. Treated fabrics continue to offer protection, even after exposure to fires and high-temperature irradiation, by the formation of a relatively tough and pliable carbonaceous fabric structure after being charred.

A new flame retardant based on APO and thiourea has recently been found to be successful for use on cottons.[17] A typical treating solution consists of 25 per cent APO, 15 per cent thiourea, a wetting agent, and 3 per cent polyethylene softener. Fabric is treated by the conventional pad-dry-cure technique. The flame resistance is excellent, and remains durable under laundering and dry cleaning. The finished fabric is also rot- and mildew-resistant and has some crease resistance.

APO is initially toxic and must be handled with care, but once the material is polymerized the end products are reported to be harmless.[17]

Techniques have been developed for imparting durable flame resistance to the surfaces of cotton textiles of low density such as cotton pile and napped fabrics. A spray technique has been used to apply the

THPC-based flame retardants. The chemical cost is reduced by using this technique, and the treated material retains its tensile and tear strength. In addition, the textile surface fibers are made more resilient.

Flame-retardant fabrics with better hand and strength result if the fabric to be treated is free of starches or sizes and is absorbent. Failure to eliminate starch causes increased stiffness and reduced wash fastness of the finish. Fabrics treated on a continuous basis are better than those produced in batches. To prevent migration of solution and stiffening of the treated fabrics, the least amount of tension possible should be applied to the fabric as it comes from the pad. Treating solutions must be kept cool, and padding must be done with a heavy squeeze-roll pressure to assure complete penetration of the fiber. Drying, which is probably the most critical operation in applying flame-retardant finishes, should be carried out below 212° F. to prevent the surface from curing before the inside of the yarn is dry. A high drying temperature causes stiffness of fabric and low tearing strengths. High air velocity also causes migration. The fabric must be dry before curing, and curing must be done immediately after drying.

What is new on the horizon? Research is continuing on the development of flame-retardant finishes with a higher phosphorus:nitrogen ratio which should improve efficiency in the process of imparting them and should be adaptable to fabrics of all weights.

Arthur[15] has shown that a free-radical mechanism is involved in the pyrolytic degradation of cotton cellulose and that, by the attachment of certain groups (aromatic) to cellulose, there is a decrease in free-radical formation. Reduction of free-radical formation should increase the flame resistance of cellulose. This fundamental information may be a lead to the development of new and better flame-retardant finishes for cotton.

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